

SUPPORTING INFORMATION FOR “Soft colloidal lithography”

Markus Weiler^{1,2} and Claudia Pacholski^{1,3*}

¹ Max Planck Institute for Intelligent Systems, Department of New Materials and Biosystems, Heisenbergstr. 3, 70569 Stuttgart, Germany

² University of Heidelberg, Department of Biophysical Chemistry, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

³ University of Potsdam, Institute of Chemistry, Am Mühlenberg 3, 14476 Potsdam OT Golm, Germany.

E-mail: cpachols@uni-potsdam.de

Experimental section

Materials and methods

N-isopropylacrylamide (NIPAM) was purchased from Sigma Aldrich and purified by re-crystallization from *n*-hexane. All other chemicals were used as received. 2-Carboxyethyl acrylate and ammonium persulfate (APS) were also obtained from Sigma Aldrich. *N,N'*-Methylene bisacrylamide (BIS), ethanol, and H₂SO₄ (p.a.) were received from Carl Roth. NaCl and H₂O₂ were supplied by Merck. Potassium persulfate (KPS) was received from Fluka. Sodium dodecyl sulfate (SDS) was supplied by Fisher Scientific. Water was deionized to a resistance of at least 18.2 MΩ [Ultra pure water system (TKA, Germany)] and then filtered through a 0.2 μm filter – referred to as Millipore water throughout the text. As glass substrates served glass cover slips (24 x 24 mm² and 24 mm x 32 mm) from Carl Roth (Germany).

SEM images were taken using a Zeiss Ultra 55 Gemini scanning electron microscope (Zeiss, Germany). Samples were coated with carbon before examination using a Bal-TEC Med020 Modular High Vacuum Coating System (Witte, Germany).

Surface topography characterization was carried out using a JPK Nanowizard 2 AFM. Surface topography was measured in air with Nanoworld NCHR cantilevers (spring constant 42 N/m, resonant frequency 320 KHz) in tapping mode.

Synthesis of polyNIPAM microgels

PolyNIPAM microgels were wet-chemically synthesized according to Pelton *et al.* (polyNIPAM spheres with a diameter of ~ 1200 nm in the swollen state) and Kim *et al.* (polyNIPAM spheres with a diameter of ~ 2100 nm in the swollen state). Briefly, the larger polyNIPAM spheres were prepared by dissolving 3.038 g NIPAM and 0.030 g BIS in 100 mL of Millipore water. The solution was filtered and stirred for 1 h at 70° C under inert atmosphere (Ar). Afterwards 0.150 g 2-Carboxyethyl acrylate (dissolved in 5 mL Millipore water and purged with Ar for 5 min) was added to the reaction solution. The polymerization was started by injecting 1 mL of an APS solution made from 0.007g APs dissolved in 10 mL of Millipore water. The reaction solution was stirred for 6 hours at ~70 °C under an Ar environment. Purification of the resulting polyNIPAM microgel was achieved by centrifugation, decantation, and redispersion in Millipore water (five times).

Synthesis of the smaller polyNIPAM colloids was achieved in the following way: 2.65 g of NIPAM and 0.1 g of BIS were dissolved in 124 mL of Millipore water. The solution was subsequently heated to ~70°C for ~ 30 min under stirring whereas the whole reaction solution was bubbled with Argon. After injection of a KPS solution (0.04 g in 4 mL deionized water) the reaction was stirred for additional 6 h at ~70 °C under an Ar environment. The resulting microspheres were purified by centrifugation, decantation, and then washed with Millipore water (at least five times).

Finally, both types of polyNIPAM colloids were filtered through an Acrodisc syringe filter with a Versapore membrane (pore size of 5 μm for the larger polyNIPAM colloids and 1.2 μm for the smaller ones). These dispersions are referred to as polyNIPAM stock solutions in the following text.

Cleaning procedure for glass substrates

Glass substrates were cleaned by immersion in piranha solution (3:1 mixture (v:v) of conc. H₂SO₄: H₂O₂ (30%)) for 2 h at least. Afterwards, the glass substrates were thoroughly rinsed with Millipore water and stored in Millipore water until use.

Self-assembly of polyNIPAM colloids at the air/liquid interface

The cleaned glass substrates were dried with compressed air. Subsequently, 100 µL of a 10% (v/v) ethanol/water mixture were then placed on a cleaned glass substrate and mixed with 4 µL of a diluted polyNIPAM stock solution (1:7 polyNIPAM stock solution : Millipore water). The self-assembly of the polyNIPAM colloids into highly ordered 2D arrays could be observed by the naked eye. For this purpose the glass substrate was illuminated from the side. The formation of hexagonally ordered arrays leads to the appearance of brilliant colors caused by diffraction of light. The degree of order of the polyNIPAM colloids assembled at the air/liquid interface was improved by shearing. For this, a pulsating gas stream was directed towards the liquid surface (gas pulse duration of approximately 1 s at a frequency of 0.2 Hz). The pulsating gas stream was maintained until a uniform diffraction pattern was formed.

Dip coating

In figure S2 the experimental set-up for depositing polyNIPAM colloidal monolayers onto glass substrates by dip coating is displayed.

First, highly ordered arrays of polyNIPAM colloids were produced at an air/liquid interface - as already been described before. The glass substrate carrying the ordered polyNIPAM colloidal monolayer was subsequently lowered into a beaker filled with Millipore water. Thereby the polyNIPAM array was transferred onto the water surface. Afterwards the beaker was placed in a heating bath (yellow). The water temperature during dip-coating was monitored using Onewire DS18B20 temperature sensors with a precision of 0.5 °C. Dip coating was carried out using a custom-made dip coater based on a Faulhaber minimotor LM1247-080-01. The cleaned glass substrate (24 x 32 mm) was retracted from the solution with a speed of ~ 0.5 mm/min. In order to prevent water condensation onto the glass substrate during the dip-coating process, an air stream was created above the glass substrate using a simple fan (indicated by the light blue arrows in the scheme).

Spin coating

Immediately after formation of a highly ordered polyNIPAM colloidal monolayer at an air/liquid, the supporting glass substrate was positioned on a spin-coater and the polyNIPAM colloids were deposited onto the glass surface by spinning.

For experiments carried out at room temperature, a Laurell WS-400B-6NPP / Lite spin coater was used. Samples were spin coated at 500 rpm for 5 min (acceleration 100 rpm/s).

For spin-coating samples at elevated temperatures a custom-made spin-coater based on a motor with a maximum rotational speed of 310 rpm was placed in a Heraeus Vacutherm VT 6025 oven (Thermo Scientific). The temperature in the oven was monitored using Onewire DS18B20 temperature sensors with a precision of 0.5 °C. The speed was controlled by a connected microcontroller and linearly increased over a period of 30 s to the maximum speed of 310 rpm. The maximum speed was maintained until the dispersion medium was completely evaporated.

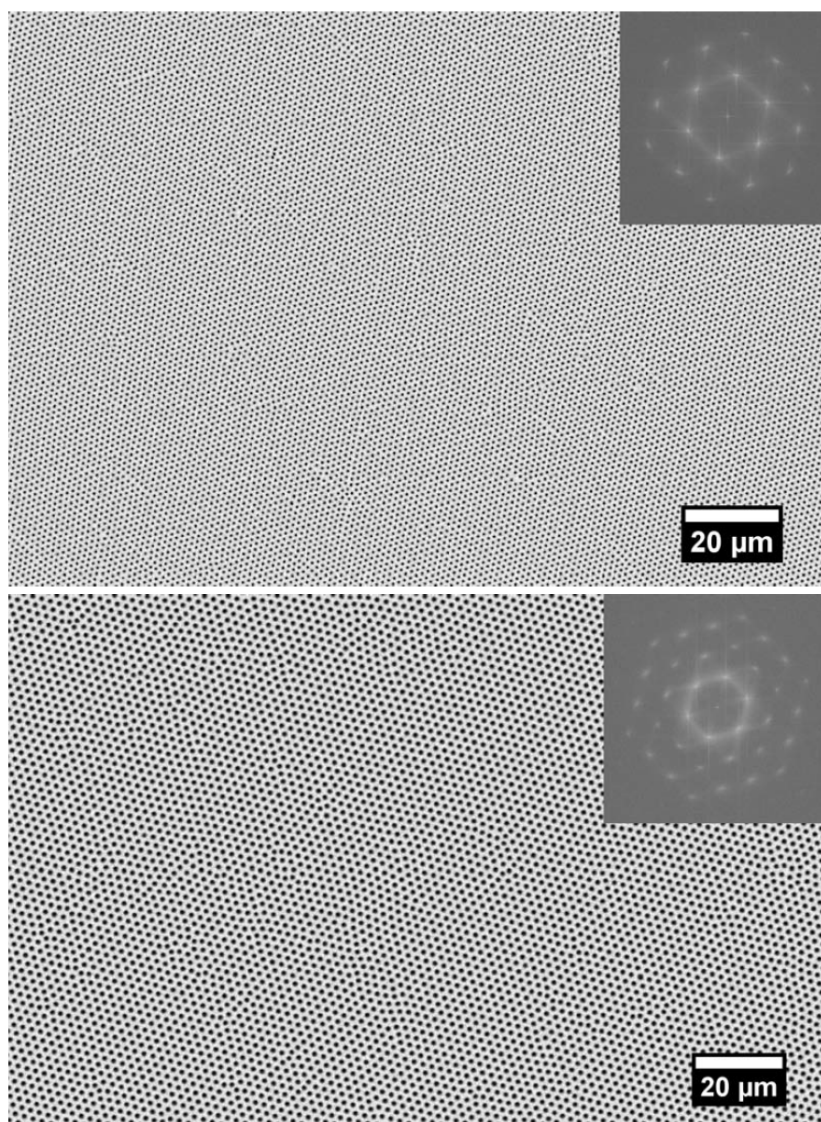


Figure S1: SEM images of polyNIPAM colloids deposited onto glass substrates at room temperature using spin-coating: a) Hexagonal lattice of polyNIPAM colloids with a periodicity of $(1.2 \pm 0.1) \mu\text{m}$ and b) hexagonal lattice of polyNIPAM colloids with a periodicity of $(2.1 \pm 0.1) \mu\text{m}$. Insets show the FFT of the respective SEM image.

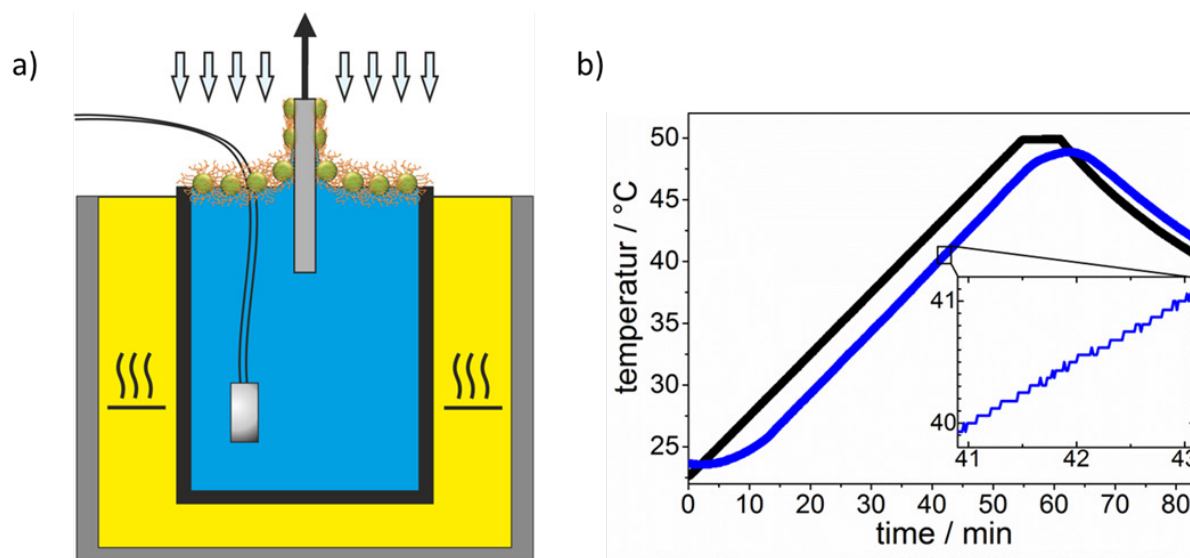


Figure S2: a) Sketch of the used dip coating set-up. The deposition temperature is controlled via a heating bath (yellow) and monitored with temperature sensors. A monolayer of hexagonally ordered polyNIPAM colloids is placed onto the water surface and transferred onto a glass cover slip (gray) by pulling it out of the water (blue). b) This graph shows how a linear temperature gradient in the heating bath (black) induces a linear temperature gradient in the liquid (blue).

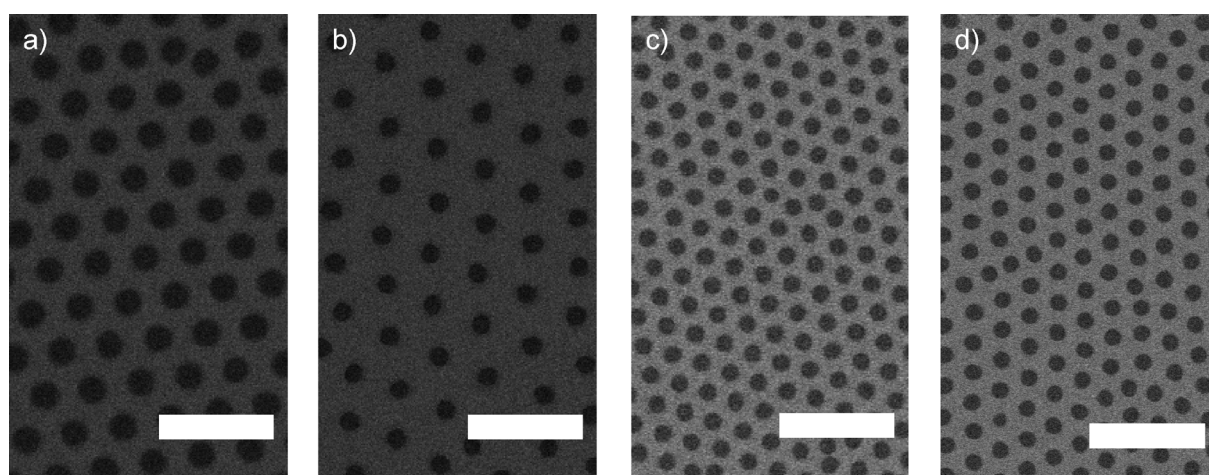


Figure S3: SEM images of polyNIPAM colloids deposited at different temperatures onto glass substrates using spin-coating: a) negatively charged polyNIPAM colloids at 40 °C, b) negatively charged polyNIPAM colloids at 60 °C, c) polyNIPAM colloids at 30 °C, and d) polyNIPAM colloids at 50 °C. Scale bar: 5 μm. The given temperature is the temperature of the oven and not of the polyNIPAM dispersion on top of the glass substrate. As the spin-coating process was started directly after closing the oven door, the exact temperature which is experienced by the polyNIPAM colloids could not be determined.

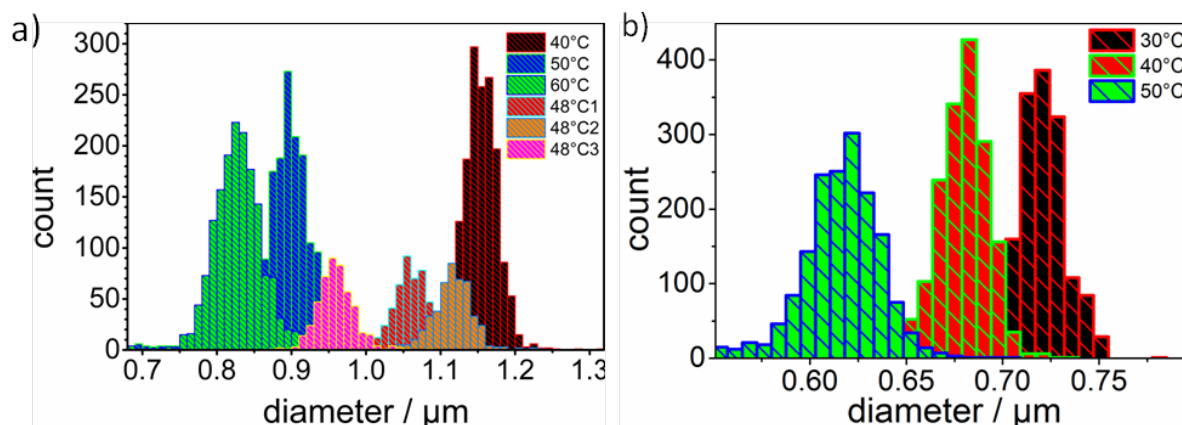


Figure S4: Histograms showing the diameter distributions of different polyNIPAM colloids spin-coated onto glass surfaces at different temperatures. a) Negatively charged polyNIPAM colloids. The large distribution of the polyNIPAM colloids deposited at 48 °C could be based either on the experimental set-up or on the LCST of the used microgel. In these experiments a custom-made spin-coater was placed in an oven. Glass substrates covered with polyNIPAM microsphere arrays pre-assembled at the air/liquid interface were placed onto the sample holder of the spin-coater. After closing the oven door the spin program was directly started. Hence, the temperature of the liquid on the glass substrate could not be precisely controlled. Moreover, in our opinion the temperature, at which the spin-coating process was carried out, was always lower than the oven temperature. b) PolyNIPAM colloids.

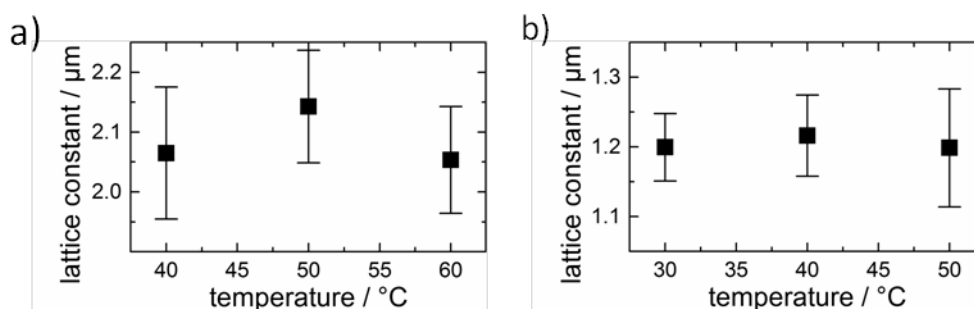


Figure S5: Lattice constants of different polyNIPAM colloids spin-coated onto glass surfaces at different temperatures. a) Negatively charged polyNIPAM colloids. b) PolyNIPAM colloids.

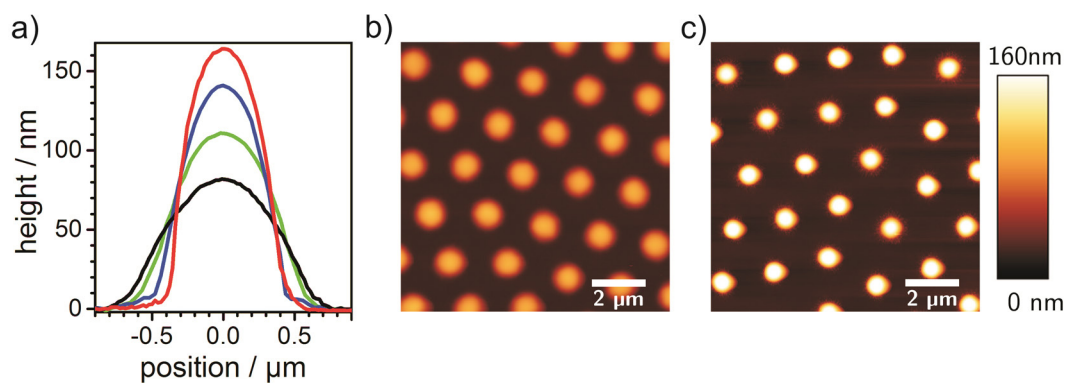


Figure S6: AFM characterization of polyNIPAM colloids deposited onto glass substrates at different temperatures. a) Cross-sectional height of a single negatively charged polyNIPAM colloid deposited onto a glass surface at different temperatures using spin-coating (black line: 30 °C, green line: 40 °C, blue line: 50 °C, red line: 60 °C). b) AFM image of negatively charged polyNIPAM colloids spin-coated at 30 °C. c) AFM image of negatively charged polyNIPAM colloids spin-coated at 60 °C.